

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Production of Acetylene and Ethylene

We, MONSANTO CHEMICAL COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 1700 South Second Street, City of St. Louis, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of acetylene and ethylene by the partial combustion of methane and/or ethane with oxygen.

While this invention is applicable to the oxidation of methane and ethane, for the sake of simplicity it will be mainly described with reference to methane. For the purpose of this invention methane and natural gas are regarded as equivalent.

It is known that by partial combustion of methane with oxygen, sufficient heat is liberated to bring about cracking of the remainder of the hydrocarbon with production of acetylene. It is also known that acetylene decomposes rather quickly at the high temperatures developed and, in consequence, it is desirable to cool the product as rapidly as possible to a temperature at which it is stable in order to obtain maximum yields.

There are a number of processes for producing acetylene from methane and other hydrocarbons by combustion. One of these, the Sachsse process, has been used commercially in Germany and a modification thereof has also been used in the United States. In the Sachsse process methane and oxygen are separately preheated to about 500°C., mixed, passed through a specially designed burner, and the effluent gases cooled. The temperature in the combustion zone reaches approximately 1400°C. and the pressure is about atmospheric. One critical operation is cooling the temperature of the effluent gases to about 80°C. within 0.01 seconds to 0.001 seconds by means of a water spray. Another critical operation is the control of the velocity of gas fed to the burner in order to avoid premature

ignition.

There are several disadvantages to the known partial combustion processes. They operate at such low pressures that the throughput is undesirably low. The mixing of preheated gases and combustion thereof in jets are very sensitive operations and unless carefully controlled are likely to result in explosions and backfiring. It is necessary to control the gas velocity and pressure very closely in order to prevent backfiring and avoid extinguishing the flame. Burner life is usually rather short. The over-all heat efficiency is rather poor since rapid cooling of the products of combustion by water removes most of the heat therefrom in a form unsuitable for preheating feed gases. Furthermore, none of the partial combustion processes give appreciable quantities of valuable hydrocarbon by-products such as ethylene.

There has been a longfelt need for increasing the capacity of plant employing conventional partial combustion processes. One conceivable way of doing this is to increase the pressure. However, even at atmospheric pressure a major difficulty has been sufficiently to quench the acetylene to suppress decomposition and polymerization thereof. If the known process was operated at superatmospheric pressure employing the known cooling means, the acetylene lost by decomposition and polymerization would be intolerable.

It is the object of this invention to provide an improved partial combustion process for the production of acetylene and ethylene from oxygen and methane and/or ethane which can be operated at pressures substantially above atmospheric pressure, thus increasing the capacity of a given size plant.

According to the present invention there is provided a process for the production of acetylene and/or ethylene by the partial combustion of methane and/or ethane in which a mixture of methane and/or ethane together with oxygen is passed, at superatmospheric pressure through a combustion zone comprising a convergent section and a divergent section in contiguous relationship and thence to

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a zone of lower pressure within such time interval that substantially no decomposition or polymerization of acetylene occurs, the ratio of the entering pressure to the exit pressure in said combustion zone being from 1.5:1 to 10:1. It is preferred that this ratio be 3:1 to 5:1.

It has been found that superatmospheric pressures can be employed materially to increase the capacity of a given plant by employing, as the means for cooling the effluent gases, a nozzle having a convergent section and a divergent section in contiguous relationship. The shape of the narrow ends of the two sections and the manner of their union are such that the inner wall of the nozzle forms a continuous smooth curve. This type of nozzle is referred to in the jet propulsion art as a DeLaval nozzle (see "Jet Propulsion and Gas Turbines" by M. J. Zucrow, page 113, 1948).

The present invention will now be described with reference to the accompanying drawings in which:

Figure 1 is a side elevation, partly in cross section, showing one form of apparatus which has been found suitable for carrying out the present invention.

Figure 2 is a front elevation view of flange 25 as viewed from the left in Figure 1.

Figure 3 is a front elevation view of flange 16 as viewed from the left in Figure 1.

In the apparatus shown in the drawings, reference numerals 1 and 2 respectively denote storage tanks for oxygen and combustible hydrocarbon. These storage tanks are respectively furnished with manually operated valves 3 and 4 and pressure regulating valves 5 and 6. The exits from valves 5 and 6 are respectively connected to conduits 7 and 8 which both lead into a mixing chamber 9. Over a substantial portion of its length chamber 9 is filled with silicon carbide granules 10, 10-U.S. standard mesh being a suitable size. The silicon carbide granules are retained in position by a steel wool retainer 11 at one end and by a foraminated plate 12 at the other end. The plate 12 is retained in position by means of a frictionally fitting retaining bushing 13 and a lip 14. The mixing chamber 9 is externally threaded at 15 and fits into a threaded boring in a flange 16. The flange 16 has a further threaded boring 28 which accommodates a thermocouple 17 and a recessed portion 29 in which is inserted a sparking plug 19. The thermocouple 17 is provided with a gauge 18. Means (not shown) are provided for energising sparking plug 19.

A second flange 25 is bolted by means of bolts (not shown) passing through openings 26 to flange 16 and is internally threaded at 24. A combustion chamber, generally denoted by numeral 20, is mounted in the internally threaded flange 25. The combustion chamber has an outlet 21, a convergent section 22, a

throat 27, and a divergent section 23. As illustrated the angle of convergence in section 22 is 60° while the angle of divergence in section 23 is 30°.

In operation oxygen from storage tank 1 and methane and/or ethane from storage tank 2 released through the valves 3, 5 and 4, 6 respectively pass along conduits 7 and 8 into mixing chamber 9 under superatmospheric pressure. Passage over the silicon carbide granules assists in securing intimate admixture of the gases prior to their entry into the combustion chamber through the foraminated plate 12. The gases are introduced in such proportions as to secure partial combustion only of the hydrocarbon or hydrocarbons present. As a rule approximately equimolar proportions of methane and oxygen or two mols of ethane for each three mols of oxygen are employed. Such proportions are conventional however and the choice thereof forms no part of the present invention.

Combustion of the entering gases in combustion chamber 20 is initiated by means of sparking plug 19. Partial combustion of the gases takes place with concomitant production of oxides of carbon and water vapour. Part of the methane is cracked to acetylene and ethylene at superatmospheric pressure and a temperature between 1150°C.—1500°C. but usually about 1200°C. Under these conditions acetylene is very unstable and the temperature must be reduced very rapidly in order to prevent most of it being lost by decomposition and polymerization. By employing superatmospheric pressure and exhausting through the outlet 21 at a substantially lower pressure we are able to effect this reduction in temperature almost instantaneously. The actual pressure is not as significant as the pressure drop. Operating under conditions such that the ratio of the pressure at the entrance of the reaction chamber to that at the exit or exhaust end of the DeLaval nozzle is from 1.5:1 to 10:1 has given good results.

Under such pressure conditions and employing the nozzle, the velocity of the gas at the throat 27 is about sonic, that before reaching the throat is sub-sonic while that in the diverging section 23 of the nozzle is supersonic. The rapid expansion of the exhaust gases through the nozzle under these high velocity conditions produces an extremely rapid cooling thereof which is essential to this invention. The order of magnitude of the rate of cooling is approximately 2.16×10^8 °C. per second. That is, the gases are cooled from about 1200°C. to about 600°C. in 2.8×10^{-5} seconds. Although the velocity depends upon a number of factors, typical velocities according to this invention (in feet per second) are 12—50 in the reaction chamber, 2600 in the throat of the nozzle, and 4500 in the exhaust from the nozzle.

In passing through the nozzle the cooling of

the effluent gases is due to the fact that the heat energy thereof is being converted into kinetic energy by expansion and acceleration. Before recovering the acetylene and ethylene from the effluent, e.g. by passage through an absorption column, the latter is decelerated to a substantially lower, subsonic velocity. This releases heat energy so that the effluent must be still further cooled. However, since the acetylene has already been stabilized, the rapid cooling initially required is no longer necessary. The additional cooling may be accomplished by spraying the effluent with water immediately after deceleration. The acetylene and ethylene are then recovered, e.g. by passage through an absorption column.

The following Examples illustrate the invention. In these the gases were separately fed into the mixing chamber 9 and ignited in the reaction chamber 20 by energizing the spark plug 19. The products of combustion were passed through the nozzle 21 into an exhaust system in which they were decelerated and

further cooled. The effluent was then analyzed for acetylene and ethylene. Details of the operating conditions and the results obtained are given in the Examples. In Examples 1—6 the gases were subjected to superatmospheric pressure in the apparatus and exhausted to atmospheric pressure. In Example 7 the gases were subjected to superatmospheric pressure in the apparatus and exhausted to four psig. In all the Examples the reaction temperature varied from about 1000°C.—1500°C. depending upon the feed gases and ratio thereof employed. Effluent composition is given in % by volume.

EXAMPLE 1.

Using the apparatus shown in the drawings a number of runs were made to determine the effect of the rate of flow of the feed gases and the length of the combustion chamber on the conversion of methane to acetylene and ethylene using a steel combustion chamber and a steel nozzle and a methane/oxygen mol ratio of 1.1:1. The following results were obtained:

Combustion Chamber Length in Inches	Flow Rate Litres/Min. @ S.T.P.	Combustion Chamber Pressure Psi	% Acetylene in Effluent	% Ethylene in Effluent
2	40	16	2.1	1.0
2	60	36	3.0	0.8
2	80	54	4.1	0.7
2	80	70	3.3	0.5
2	100	96	1.6	0.2
2	120	125	1.2	0.3
1	40	31	3.5	0.7
1	60	50	4.3	0.9
1	100	103	3.9	0.6
1	120	130	2.3	0.4
0	80	49	4.7	0.8
0	100	78	4.3	0.5
0	120	92	3.5	0.3

EXAMPLE 2.

Using the apparatus shown in the drawings a number of runs were made to determine the effect of the mol ratio of methane to oxygen and length of combustion chamber on the con-

version of methane to acetylene and ethylene using a steel combustion chamber and steel nozzle and a flow rate of 80 litres per minute. Specific details are tabulated below.

Combustion Chamber Length in Inches	Mol Ratio Methane: Oxygen	Combustion Chamber Pressure Psi	% Acetylene in Effluent	% Ethylene in Effluent
2	0.9	63	trace	0.0
2	1.0	50	2.6	0.2
2	1.1	54	4.1	0.7
2	1.2	41	2.8	1.1
2	1.4	32	1.4	1.3
1	0.9	104	trace	trace
1	1.0	92	1.0	0.1
1	1.1	90	3.3	0.5
1	1.2	62	1.4	0.8
1	1.4	56	1.2	0.9
0	1.0	48	3.9	0.7
0	1.1	49	4.7	0.8
0	1.2	48	3.5	1.1
0	1.3	48	2.7	1.3

In Examples 1 and 2 above it will be noted that the runs were made in a steel combustion chamber and a steel nozzle. It was found that under the high temperature conditions prevailing deformation of the exhaust system occurred. This was avoided by spraying water into the exhaust system downstream just beyond the exit end of the diverging section of the nozzle. Further downstream the effluent was decelerated and cooled with water. In Examples 3—6 no cooling was necessary because a silicon carbide combustion chamber and nozzle were used. However, the effluent gases were decelerated and then cooled with water as in Examples 1 and 2.

EXAMPLE 3.

From Examples 1 and 2 it might be contended that the water spraying effected a substantial part of the initial cooling and there-

fore that the nozzle alone was insufficient to effect the cooling. To determine that this was not so the run tabulated below was made without employing water spraying or anything except the nozzle to accomplish the initial cooling. It was necessary to make the combustion chamber and nozzle of material which would withstand the high temperature conditions: silicon carbide was selected and found to be satisfactory. The length of the reaction chamber was 4.5 inches. To enable the combustion chamber and nozzle to withstand the pressures developed and to facilitate fabrication, they were placed inside an iron pipe and held therein by means of silicon carbide cement and conventional flanges, the other parts of the apparatus being substantially as shown in Figure 1 of the accompanying drawing. Specific details are tabulated below.

Mol Ratio Methane: Oxygen	Flow Rate Litres/Min. @ S.T.P.	Combustion Chamber Pressure in Psi	% Acetylene in Effluent	% Ethylene in Effluent
1.1	80	27	4.8	0.7

EXAMPLE 4.

The following runs were made to determine the effect of magnitude of nozzle angles on the conversion of methane to acetylene and ethylene using a rate of flow of 80 litres per

minute and the apparatus described in Example 3 except that the angles of the nozzle were varied. Specific details are tabulated below.

Total Angle of Convergence Degrees	Total Angle of Divergence Degrees	Combustion Chamber Pressure in psi	Mol Ratio Methane: Oxygen	% Acetylene in Effluent	% Ethylene in Effluent
25	18	27	1.1	4.8	0.7
18	25	24	1.1	1.6	0.1

EXAMPLE 5.

The following runs were made to determine the effect of preheating the feed gases. Methane was used in the first run and natural gas in the second run. The natural gas used contained 92% of methane and 5% of ethane

by volume. A flow rate of 80 litres per minute and a methane/Oxygen mol ratio of 1.1 were used. The runs were carried out in the apparatus described in Example 3 above. Specific details are tabulated below.

Preheat °C.	Combustion Chamber Pressure in psi	% Acetylene in Effluent	% Ethylene in Effluent
None	27	4.8	0.7
540	16	5.4	0.5

EXAMPLE 6.

This Example shows the use of ethane instead of methane. The feed gases were pre-

heated to 600°C. and the apparatus described in Example 3 was used. Specific details are given below.

Mol Ratio Ethane: Oxygen	Flow Rate Litres/Min. @ S.T.P.	Combustion Chamber Pressure psi	% Acetylene in Effluent	% Ethylene in Effluent
0.7	30	15	2.5	25

EXAMPLE 7.

The purpose of this Example is to show exhausting to superatmospheric pressure using

the apparatus described in Example 3. Specific conditions and results are tabulated below.

Mol Ratio Methane: Oxygen	Flow Rate Litres/Min. @ S.T.P.	Pressure—psi		% Acetylene in Effluent	% Ethylene in Effluent
		Combustion Chamber	Exhaust		
1.0	80	16	4	5.3	0.7

Whilst the above Examples illustrate exhausting the gases only at atmospheric and superatmospheric pressures, it is nevertheless possible to exhaust at subatmospheric pressures

provided that the pressure ratio is maintained within the limits herein specified. The advantages of operating under pressure are that it increases the capacity and renders the process

less sensitive to fluctuations in pressure, i.e. it makes tolerable relatively large variations in pressure without causing explosions, back-firing, or flame extinction. The particular pressure ratio employed will depend in part upon the temperature, nozzle diameter, flow rate, and the materials from which the apparatus is constructed.

The diameter of the throat of the nozzle is not critical. Under any given set of operating conditions with the size of the other parts of the apparatus fixed, the diameter of the throat will determine the pressure ratio.

The temperature varies inversely with the methane/oxygen ratio and is normally from 1150°C. to 1500°C. Any desired operating temperature within this range can be attained by varying the methane/oxygen ratio alone or in conjunction with preheating the feed gases. Thus, preheating the feed gases compensates for the reduced temperatures resulting from higher methane/oxygen ratios. One advantage of using a high ratio in conjunction with preheating is that it gives a higher concentration of acetylene in the effluent gases. If preheating is employed the effluent gases, as they leave the nozzle, may be utilized to heat the feed gases.

The rate of flow may be varied widely, but it must be such that the velocity of the gases in the combustion chamber is less than the velocity of flame extinction and the velocity of the feed gases at the point of entry into the combustion chamber must at least equal the velocity of propagation of a flame through the gaseous mixture.

The acetylene produced has been expressed as a percentage by volume of acetylene in the effluent gases: this is conventional since it is a measure of the efficiency of the process. In addition, it may however be expressed as the actual yield of acetylene, when it is based either on the methane charged to the reaction or on that consumed in the reaction. The theoretical maximum yield is approximately 35% by volume. According to the present invention the yields of acetylene are about 20%—25% by volume based on the methane charged and about 28%—31% by volume based on the methane consumed. The use of

ethane gives substantially higher yields of ethylene than does the use of methane. When methane is used the yields of ethylene may vary from a trace up to about 5% by volume based on the methane charged and from a trace up to about 7% by volume based on the methane consumed. By using ethane a yield of about 50% of ethylene was obtained based upon the ethane consumed.

What we claim is:—

1. A process for the production of acetylene and/or ethylene by the partial combustion of methane and/or ethane in which a mixture of methane and/or ethane together with oxygen is passed, at superatmospheric pressure, through a combustion zone comprising a convergent section and a divergent section in contiguous relationship and thence to a zone of lower pressure within such time interval that substantially no decomposition or polymerization of acetylene occurs, the ratio of the entering pressure to the exit pressure in said combustion zone being from 1.5:1 to 10:1.

2. A process according to Claim 1 in which the ratio of the entering pressure to the exit pressure in said combustion zone is 3:1 to 5:1.

3. A process according to either of Claims 1 or 2 in which the mixture of gases is heated prior to being passed to said combustion zone.

4. A process according to any of the preceding Claims in which the effluent gases are exhausted from said combustion zone to a superatmospheric pressure.

5. A process according to any of the preceding claims in which the effluent gases are decelerated and further cooled with water prior to passage to absorption of acetylene and/or ethylene.

6. A process for the production of acetylene and/or ethylene substantially as hereinbefore described with reference to the accompanying drawings.

7. Acetylene and/or ethylene whenever produced by the process of any of the preceding Claims.

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